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SEAWEEDS AND THEIR USES

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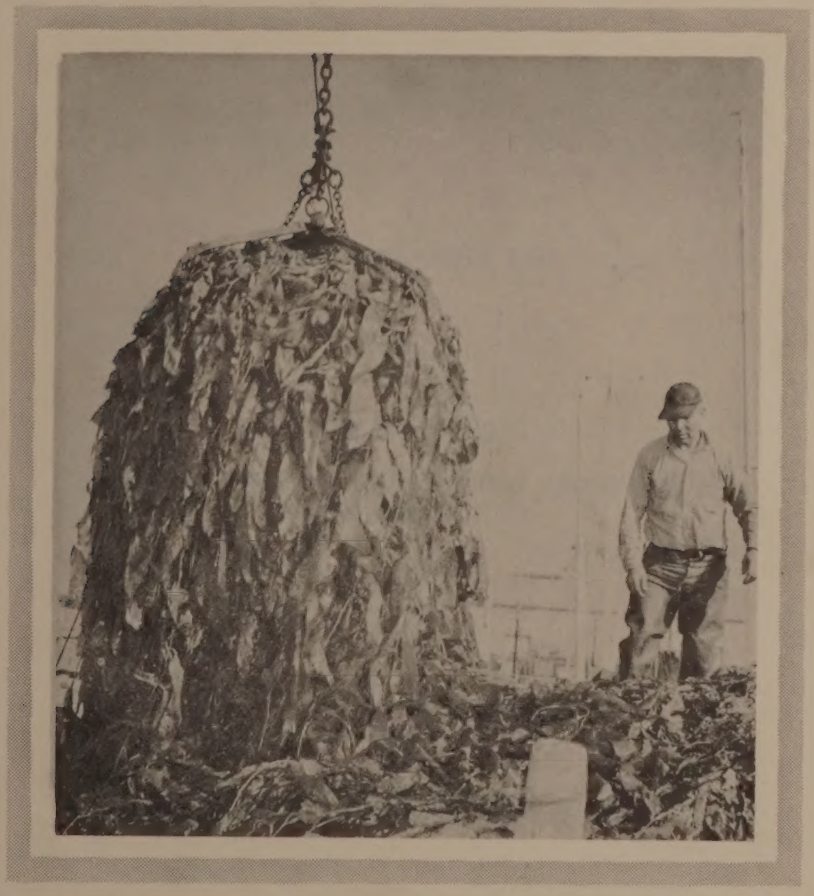

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SEAWEEDS AND THEIR USES

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Photograph courtesy Philip R. Park, Inc., Naval Station, San Pedro, California.

INTRODUCTION

Seaweeds are misnamed, for they are not weeds but highly useful plants that yield a number of products having many important uses. The products obtained from the seaweeds may be divided into two groups: natural and derived.

The natural products are those in which the seaweed itself is used as the end product. These may be whole, ground, or dried. Such products are used primarily for human food, for animal food, and for fertilizer.

The derived products are those manufactured from seaweeds by chemical processes. Historically these products have included a wide variety of materials, such as iodine, acetone, and decolorizing carbon. The major derived products, both in the present and in the recent past, are those that have the ability to form gels and colloidal suspensions. In the United States, the principal colloidal products made from seaweeds are agar, algin, and carrageenin. Commercially these derived products are vastly more important than are the natural ones.

CLASSIFICATION

Seaweeds, which are marine algae, ordinarily are classified according to color: green, blue-green, brown, and red. The scientific names for these four kinds of algae are as follows:

1. Green - - - Chlorophyceae
2. Blue-green - - - Cyanophyceae
3. Brown - - - Phaeophyceae
4. Red - - - Rhodophyceae

HABITS OF GROWTH

The habits of growth of the algae vary quite widely as can be seen from the following discussion in which the habits of each of the four kinds are described.

Green and Blue-Green Algae

The green algae are found both in fresh and in salt water. Some varieties grow on trees and in other terrestial locations. The marine forms are better developed than are the fresh-water forms. The blue-green algae also are found both in fresh and in salt water. In contrast to the green algae, the fresh-water forms are the more common, often being found in stagnant water. In general, the green and the blue-green algae are relatively small plants, which descend in size and complexity to unicellular organisms.

Brown Algae

The brown algae grow best in the colder waters of the oceans.

Some of the larger forms are called rockweeds because they cover rocks between the low- and high-tide levels. Other of the larger forms are called kelps. These grow below or just at the low-tide levels and sometimes form large beds. The larger forms can withstand the battering of heavy surfs because of their firm texture and strong holdfasts. The smaller forms generally grow in quiet waters and are membranous or cord-like.

Red Algae

The red algae in general flourish in warmer waters than do the brown seaweeds. Also, they are usually found in deeper waters, some of the forms growing at depths of 200 feet or more, the depth limit varying with the clearness of the water. Since most of the red seaweeds seem to prefer shaded locations, it is probable that their characteristic color is associated with their habit of growing where the light is subdued.

METHODS OF HARVESTING

Although some seaweeds, such as the giant kelp, are easily harvested by mechanical means, many of the seaweeds, such as the Gelidia, must be collected by hand. Thus, the development of mechanical harvesters poses one of the fundamental problems of the seaweed industry.

The Scottish workers have given much study to the development of a high-capacity mechanical harvester (Jackson 1949). One piece of equipment on which they have worked consists essentially of two side chains with steel mesh stretched between them to form a continuous belt. Short hooks are mounted at suitable intervals. The purposes of the steel mesh are (1) to compact the weed in front of the hooks and (2) to cause the trailing end of the gear to ride on the surface of the weed bed and thus prevent the hooks from fouling. The downward thrust of the trailing end on the seabed is reduced by means of floats. To prevent anchoring of the hooks or chains on obstructions on the seabed, the operators run the belt in the reverse direction to the travel of the boat.

CONSTITUENTS

The major constituents in seaweeds are the carbohydrates which, at least in the brown seaweeds, are primarily mannitol, laminarin, and the cell-wall substances--alginic acid, cellulose, and fucoidin. The minor constituents include protein, fat, minerals, and vitamins (Woodward 1951).

Some of the seaweeds contain a fair amount of protein, but the fat content, in general, is quite low. The seaweeds are a good source of minerals. In fact, during World War I, they were a commercial source of iodine and of potassium chloride. The seaweeds contain all the mineral elements required for growth.

Seaweeds are also a good source of vitamins. These include beta-carotene (which is converted to vitamin A in the body), thiamin, riboflavin, niacin, pantothenic acid, vitamin B_{12}, vitamin C, and vitamin D.

NATURAL PRODUCTS

As was stated in the introduction, the natural products obtained from seaweed are used principally for human food, for animal food, and for fertilizer.

Human Food

The Oriental peoples, particularly the Japanese, have long used seaweeds for human food. This use in the United States, however, has been quite limited. The species employed principally for food in this country are Irish moss (Chondrus crispus), dulse (Rhodymenia palmata), and purple laver (Porphyea perforata).

Irish moss is used, mostly in the New England States, for making blancmange. Dulse is used commercially as a thickener in soups, sauces, and gravies. It is also used in salads and in relishes. For these latter purposes, it has been made available on the retail market, packed in cellophane. Purple laver has been used in this country primarily by the Chinese for the preparation of seaweed soup.

Inasmuch as seaweeds are not as digestible and palatable for most Western people as are vegetables, the seaweeds are not likely soon to become as popular a food item in the United States as they are in the Orient. Ash (1954) has suggested that the Oriental peoples may have developed an intestinal flora capable of digesting the seaweed carbohydrates.

The fresh-water green alga chlorella has excited interest recently, since it has been found high in protein. It therefore may have potential value as a food. The problems involved, however, in producing and in marketing such a product are tremendous. With the available supplies of competing protein foods of proved acceptability from other sources, an attempt to produce a foodstuff from chlorella and market it in the United States would meet with great difficulties.

Animal Food

Seaweed has found considerable use in Europe as an animal food. On the coast of Ireland, sheep are said to eat seaweed even when grass is available.

The meal made from seaweed can be used as a feed, but the salt content is very high. To overcome this difficulty, some of the manufacturers dissolve out the excess salt. Some also caramelize the sugars to remove the characteristic odor of the meal, which cattle seem to dislike.

From 10 to 20 percent of seaweed meal can be included in the diet of sheep, pigs, and horses, and up to 10 percent of the meal can be included in the diet of poultry. Cows usually do not find the meal palatable, but some cows will eat it. At the foregoing levels in the diet, the inclusion of seaweed meal does not apparently affect the flavor of the meat or of the dairy products.

In the United States, most of the seaweed meal is produced in California. One of the firms there has manufactured a product in which the seaweed meal is combined with fish meal and fish solubles.

Fertilizer

Macpherson and Young (1949) found that in the common seaweeds of the Maritime Provinces, the nitrogen content was 2.40 percent and the phosphorous content was 0.24 percent, on the dry basis. (The moisture content of the seaweeds averaged 83.0 percent.)

Although all of the seaweeds are relatively low in nitrogen and in phosphorous, they are high in potassium and in the trace elements. Suitably supplemented, the seaweeds therefore make good fertilizers. An advantage of seaweeds over many other organic materials is that they are free of weed seeds and spores of crop diseases.

Seaweeds have been used extensively in Europe and Asia as a fertilizer, but they have found only limited use for this purpose in the United States. The principal geographical sections in which seaweed has been put to this use have been the New England States and California. In 1951, a firm located in Portland, Oregon, was started for the purpose of producing a dried meal from seaweed collected on the Oregon coast. It, however, was not a successful business venture, owing in part no doubt to the difficulty of collecting the seaweed.

DERIVED PRODUCTS

The derived products include (1) those obtained from seaweeds during World War I, (2) mannitol, and (3) phycocolloids.

The products obtained from seaweeds during the first world war are no longer produced, but they are at least of historical interest because they show some of the many products that can be made from seaweeds--if economic conditions are favorable.

Mannitol is one of the products that have been commanding considerable attention of late, particularly from the Scottish chemists.

The phycocolloids give seaweeds their present primary economic value.

The Greek term for seaweed is "Phykos." Thus, "phycocolloid" is a convenient name for the colloidal materials obtained from seaweed. Tseng (1945) has defined phycocolloids as the polysaccharides that are derived from brown or from red seaweeds and that are capable of forming colloidal systems when dispersed in water.

A polysaccharide is one of the carbohydrates. The carbohydrates, in turn, are classified as monosaccharides, disaccharides, trisaccharides, tetrasaccharides, and polysaccharides. Most of the monosaccharides in nature are pentoses ($C_5H_{10}O_5$) or hexoses ($C_6H_{12}O_6$). The polysaccharides contain more than four molecules of the simple carbohydrate combined together: $(C_5H_8O_4)n \cdot H_2O$ or $(C_6H_{10}O_5)n \cdot H_2O$ in which n is large. Thus, with the phycocolloids, we are dealing with molecules that are both large and complex.

For our purpose, a colloid can best be defined by example. Some of the common colloidal materials are albumin, gelatin, and starch. In general, the colloidal materials are characterized by having large molecules.

Products Obtained During World War I

During World War I, the California kelp industry produced acetone, ethyl acetate, ethyl propionate, ethyl butyrate, iodine, potassium chloride, sodium chloride, and a decolorizing carbon called "Kelpchar." Some 10 factories were engaged in this manufacture. They all shut down following the War, however, as their products could then be obtained more cheaply from other sources.

The processes used in California at that time have been described by Wohnus (1942). There were two processes: (1) the char and (2) the fermentation. The char process produced decolorizing carbon, sodium chloride, potassium chloride, and iodine. The fermentation process, which was developed by the Hercules Powder Company after much research, produced acetone and the other solvents listed above, in addition to iodine and potassium chloride.

Although the seaweeds are no longer a commercial source of iodine or of potassium chloride in the United States, future developments may once again change this situation. Cameron (1915) has estimated that Pacific kelps of the United States could, if necessary, furnish over 6,000,000 tons of potassium chloride and 19,000 tons of iodine per year.

Analyses show that the kelp, Nereocystis, from the Puget Sound area contains about 30.9 percent potassium chloride and 0.14 percent iodine, on the dry basis.

Mannitol

Mannitol is an alcohol having 6 OH groups. One of the uses for d-mannitol is in the manufacture of an explosive, which is produced from

it by nitration (Anderson 1947). Other uses for it are in foodstuffs and in a dusting powder for chewing gum as well as in the manufacture of varnishes, coatings for fancy papers and leathers, shoe polishes, soldering fluxes, and pharmaceutical products such as metal complexes and colloidal suspensions (Jackson 1949).

Black (1948) has pointed out that in the seaweeds, mannitol seems to be a primary product of photosynthesis; the mannitol accumulates in the frond during the summer. Minima in the mannitol content of the stipes (stems) occurs during the spring when there is little photosynthesis. The plant should be dried as soon as it is collected so that the mannitol cannot be used to synthesize protein.

Black, DeWar, and Woodward (1951), in a study of four species of brown seaweed, found that the mannitol content varied from 9.1 to 25.5 percent, on the dry basis.

Many of the studies on mannitol have been made by the Scottish chemists. American chemists so far have shown relatively little activity in this field, which would indicate that no appreciable American production is to be expected in the near future.

Phycocolloids

The phycocolloids can be divided into those of minor and of major economic importance. The phycocolloids of present minor importance are:

1. Laminarin
2. Fucoidin
3. Funorin
4. Miscellaneous phycocolloids such as agaroid, iridophycin, and others described by Tseng (1945) and Stoloff (1954).

The phycocolloids of major economic importance are:

1. Agar
2. Algin
3. Carrageenin

Laminarin

Laminarin is a reserve carbohydrate in kelps that is analogous to starch in land plants. Its empirical chemical formula $(C_6H_{10}O_5)_n$ is the same as that for starch, but its structure is different.

Black (1950), in studies of Laminariaceae, found that laminarin was present only in the frond. The laminarin could be isolated in two forms: (1) an almost water-insoluble form from Laminaria cloustoni, which separates from cold water, and (2) a more soluble form from Laminaria digitata, which can be obtained from aqueous solution on the addition of an alcohol.

Friedlaender, Cook, and Martin (1954)--from sedimentation, diffusion, and viscosity measurements--estimated that the molecular weight of soluble laminarin from Laminaria digitata was about 5,300, and that the molecular weight of the insoluble form from Laminaria cloustoni was about 3,500. Both forms of laminarin were poly disperse. Mild methylation of the laminarin from Laminaria cloustoni decreased the molecular weight and increased polydispersity.

Particle size is of interest because of the possible use of sodium laminarin sulphate as a blood anticoagulant and of hydroxyethyl laminarin as a plasma substitute.

Laminarin can be obtained as a byproduct in the manufacture of sodium alginate. The laminarin is soluble in calcium chloride solution and is obtained by evaporating the solution to a small volume and then precipitating the laminarium with 85-percent alcohol. The precipitated laminarin can be purified by redissolving it in calcium chloride solution and then using alcohol to reprecipitate it.

Fucoidin

Fucoidin is the principal polysaccharide sulfate ester of the brown seaweeds. It differs from that of the red seaweed in that the main carbohydrate skeleton is founded on fucose instead of on galactose.

Percival and Ross (1950) obtained fucoidin from various species of seaweed by extraction with hot water and removal of alginates and proteins with lead acetate and barium hydroxide. The resulting lead hydroxide-fucoidin complex then was decomposed with dilute sulfuric acid, and the polysaccharide was isolated after dialysis, treatment with Filter Cel, and precipitation from ethanol.

They found that the main inorganic ion was calcium. A typical analysis gave calcium, 25.0 percent; magnesium, 1.9 percent; sodium, 1.1 percent; potassium, 0.8 percent; and sulfate, 73.2 percent.

Funorin

Funorin is the polysaccharide obtained principally from funori, the dried material prepared by the Japanese from Gloiopeltis furcata. Funorin is a gluey material; it has long been used in the Orient for sizing textiles.

Agar

Of the three major phycocolloids manufactured in the United States, agar is the one produced in least quantity. Although it accounts for only a very minor part of the financial income from the phycocolloids manufactured here, it nevertheless is highly important. It was, in fact, one of the strategic materials during World War II, owing to certain of its unique gel-forming properties.

Use.--Agar is used for bacteriological, medicinal, dental, and industrial purposes and is manufactured in grades to correspond.

The bacteriological grade is used in the preparation of microbiological cultures and in orchid growing, research in physical and colloidal chemistry, photography, pharmacy, and topical medicine. The use of agar in the preparation of solid culture media in bacteriology is one that made it a strategic product when the supply of agar from Japan was cut off during World War II.

The medicinal grade of agar is used as a laxative, as an ingredient in health foods, and as an emulsifier.

The dental grade is used in making hydrocolloidal impressions in dentistry and moulages in art and criminology. It is also used in emulsions; storage-battery separators; fining of wines and juices; sizing of luxury fabrics; and lubricants for drawing tungsten, tantalum, and molybdenum wires.

The industrial grade is used for canning jellied fowl, fish, and meat; for stabilizing sherbets and ices, cheeses, and bakery products; for the making of candy and conserves; and for all gelatin uses requiring a stabilizer of non-animal origin.

Agar is a convenient jelling agent in home cooking. Since it is low in digestible carbohydrate (and calories) and is not derived from animal sources, it is useful in diets limited by health or religious considerations.

Source.--On the East Coast, the principal species of seaweeds used in the production of agar (Humm 1951) have been Gracilaria confervoides, Gracilaria foliifera, and Hypnea musciformis. The producing areas are the coasts of North Carolina and Florida. These seaweeds grow in shallow water and can be collected by being raked aboard a skiff. In the fall, they can be obtained from the beaches when washed ashore. Although a small amount of these seaweeds was collected during World War II, this area is no longer in production.

On the West Coast, the principal species used was Gelidium cartilagineum, although Gelidium arborescens and Gelidium nudifrons have been used to a limited extent. The producing areas are Southern California and Lower California.

Gelidium cartilagineum grows on rocks in fast-moving water. The other two species are found in somewhat deeper water to a depth of about 80 feet below the surface. These species of seaweed are usually collected by skin divers or by divers using regular diving suits. In general, the Gelidia are most valuable when harvested during the warmer months.

The seaweed--if spread out on the beach, on grass, or on racks; washed with fresh water daily; and turned daily--will bleach in from 4 days to 2 weeks. Although this treatment increases the value of the product, where labor is scarce and costly, the harvested seaweeds can be given a single fresh-water wash and then dried in the sun without further treatment other than turning.

The seaweed, when thoroughly dry, is pressed into bales of 200 pounds, bound securely with wire, and shipped to the processors. If the plants contain more than 20 percent moisture, they will decompose during transportation or upon storage.

Selby[1/] has pointed out that agar weeds vary greatly in value. Thus, some are too low in agar to be worth harvesting, whereas others are worth upwards of $350 per ton, f.o.b. San Diego. The value is determined by analysis.

Each shipment must pass certain specifications. The moisture content must not exceed 20 percent. The gelatin temperature of a 1.5 percent solution must not exceed 39° C. The gel strength must not be poorer than 0.17 percent (the larger this percentage, the poorer the gel, since the percentage is determined by the amount of sample required to give a gel of standard strength), and the melting temperature of a 1.5 percent solution must not be less than 80° C. If the shipment meets these specifications, payment is made on the basis of agar content and gel strength. The harvested Gelidia yield agars having gel strengths of 0.08 to 0.125 percent, the percentage varying with the species, season, and latitude.

Method of manufacture.--Tseng (1945)(1947) has reported on the process of agar manufacture as used in California. This process is based on the fact that agar is soluble in hot water but much less soluble in cold. Although the costs of producing agar are high in the United States, the agars produced here are of such excellent quality that they are able to compete with those from other countries.

Properties.--The properties of agar can be considered from three aspects: (1) the properties of the various grades of agar, (2) the properties of agar that make it suitable for use as a culture medium in bacteriology, and (3) the properties of the various agar gels as indicated by gel strength.

1/ H. H. Selby, Personal communication, 1955.

1. Grades: The properties of the various grades of agar are as follows:

A. Bacteriological grade
   (1) High clarity in solution
   (2) Freedom from heat-resistant organisms
   (3) Low content of metabolizable and inhibiting impurities
   (4) Freedom from debris
   (5) Good surface hardness and resilience of gel for adequate streaking characteristics
   (6) Quick solubility

B. Medicinal grade
   (1) Good color
   (2) Absence of taste and odor
   (3) High fluid absorption (13 to 30 times)
   (4) Freedom from irritants

C. Dental grade
   (1) Very high gel strength
   (2) Very high gel resilience
   (3) Freedom from heat-resistant organisms
   (4) Freedom from plaster-set inhibitors
   (5) Freedom from insolubles
   (6) High solubility
   (7) Good stability

D. Industrial grade: The industrial grade is identical with the bacteriological grade except that the clarity of solution is not so high.

2. Culture medium: The remarkable properties of agar that make it ideal as a solid culture medium in bacteriology are as follows:

A. Melted agar remains liquid at as low a temperature as about 32° to 39° C.

B. The resulting fluid has low viscosity.

C. After being cooled below 32° to 39° C., the fluid changes to a gel that remains semisolid at as high a temperature as 85° to 100° C.

D. Agar is nearly transparent and is nearly neutral in reaction.

E. Few common bacteria digest agar.

3. Gel strength: The commercial agars have gel strengths that vary from 0.065 to 0.50 percent (Selby 1955) and are rated as follows:

A.	Up to 0.10 percent	--	exceptionally fine
B.	0.10 to 0.14 percent	--	excellent
C.	0.14 to 0.20 percent	--	good
D.	0.20 to 0.25 percent	--	fair
E.	Over 0.25 percent	--	poor

Algin

Algin is the phycocolloid manufactured in greatest quantity in the United States. It accounts for more than half of the financial income from the phycocolloids produced here. A significant factor in this production is the ease of harvesting the seaweed from which the algin is made.

Use.--Algin products find use primarily in (1) foods, (2) pharmaceutical and cosmetic preparations, and (3) industrial applications, as follows:

1. Foods:
   - A. Dairy products
     - (1) Ice cream
     - (2) Dry ice cream mix
     - (3) Sherbet
     - (4) Chocolate milk
     - (5) Chocolate toddy
     - (6) Sterilized cream
     - (7) Cheese
   - B. Other food products
     - (1) Bakery icings and meringues
     - (2) Salad dressings
     - (3) Frozen foods
     - (4) Fountain syrups
     - (5) Orange concentrates
     - (6) Candy
     - (7) Pudding

2. Pharmaceutical and cosmetic preparations:
   - (1) Aureomycin tablets
   - (2) Terramycin suspensions
   - (3) Penicillin suspensions
   - (4) Sulfa suspensions
   - (5) Triple sulfa tablets
   - (6) Anti-acid tablets
   - (7) Aspirin compound tablets
   - (8) Calamine lotion
   - (9) Hemostatic powders

(10) Bulking laxatives
(11) Toothpaste
(12) Dental impression compounds
(13) Surgical jellies
(14) Mineral oil emulsions
(15) Suppositories
(16) Orthopedic impression compounds
(17) Rubbing ointment
(18) Shaving cream
(19) Hand lotion and creams
(20) Wave lotion
(21) Shampoo

3. Industrial applications:
   A. Rubber
      (1) Natural and synthetic laxtex
      (2) Creaming and thickening
      (3) Automobile carpeting
      (4) Babies rubber pants
      (5) Foam coatings
      (6) Rubber coatings
      (7) Tires

   B. Textile products
      (1) Size compounds for cotton and rayon
      (2) Textile print pastes
      (3) Plastic laundry starch

   C. Adhesives
      (1) Wall board
      (2) Paper bags
      (3) Shipping containers
      (4) Gummed tape
      (5) Decals

   D. Paper products
      (1) Food packages
      (2) Pharmaceutical soap and detergent packages
      (3) Milk containers
      (4) Butter cartons
      (5) Frozen food packages
      (6) Insulation board
      (7) Food wrappers
      (8) Greaseproof paper
      (9) Acoustical tile

   E. Other industrial products
      (1) Paints
      (2) Ceramic glazes
      (3) Porcelain ware
      (4) Leather finishes

(5) Auto polishes
(6) Welding-rod coatings
(7) Boiler compounds
(8) Battery plate separators
(9) Wallboard joint cement
(10) Beet sugar processing
(11) Wax emulsions

Source.--Most of the algin produced in the United States is derived from the giant kelp (Macrocystis pyrifera) obtained off the coasts of California and Lower California. Smaller quantities of broadleaf kelp (Laminaria sacchrina) and horsetail kelp (Laminaria digitata) on the North Atlantic also are used.

The beds of giant kelp are of enormous size, some being as much as 2 square miles in area. The kelp grows on rocky bottom (the base must be substantial enough to resist the pull of the growing float bulbs) outside the breaker area in water from about 30 to 90 feet deep.

In the reproductive cycle, spores are released throughout the year from the lower fronds of the kelp. The spores attach themselves to some hard surface and then germinate and grow into small filament-like plants of microscopic size. Eggs released by the female plant are fertilized by free-swimming sperms from the male plants. The fertilized eggs develop at an exceedingly rapid rate to become the plant, which grows to the surface in only a few months.

Owing to the habits of growth of the giant kelp, the harvesting can be done mechanically. A large mowing machine, the cutting bar of which is set about 4 feet below the surface of the water, is operated from the front end of a motor-driven barge. As the kelp is cut by the mowing machine, it is brought aboard the barge by means of a conveyor. As much as 300 tons of kelp a day can be harvested in this manner (Tseng 1947).

The harvesting is done under the strict regulation of the California Fish and Game Commission, which governs the depth of cutting and other procedures. Only the mature beds are cut.

The fronds of the mature plants, if not harvested, would break loose from the parent plant and rot in the water or drift up on the beaches. Harvesting removes the dense mat of material on the surface, allowing light to reach the immature fronds. Their growth is thus stimulated, and new fronds rapidly replace the harvested plants. Plants cut back in this way will grow, within a few weeks, new leafy fronds as long as 20 feet. There thus is no danger of depletion.

This method of harvesting has an additional value in that it reduces the amount of giant brown kelp washed onto the recreational beaches from these beds. Since the kelp, when rotting on the shore, accumulates flies and is odoriferous, its presence on a recreational beach is objectionable.

The masses of kelp found along the shores of Lower California, in areas where kelp is not harvested, show the beneficial effect of judicious harvesting.

Method of manufacture.--The giant kelp contains salts, laminarin, and mannitol, which must be separated from the algin. This separation is made on the basis that alginic acid and the alginate salts of polyvalent metals are insoluble.

A number of different processes of manufacture have been used, as described by Humm (1951), Stoloff (1954), and Tseng (1947).

Properties.--Algin solution decreases in viscosity by about 15 percent with each 10° F. rise in temperature. This change in viscosity is reversible. That is, the solutions regain their viscosity when cooled. If the solutions are held at high temperatures for a prolonged time, however, the viscosity may decrease, owing to a partial depolymerization of the algin molecule.

The addition of about 10 to 25 percent of alkaline phosphates or carbonates, by wieght of algin, improves the smoothness and the flow properties of algin solutions and decreases the viscosity. Such additions form a convenient method of raising the pH. The addition of strong alkalis to an algin solution has no immediate effect below a pH of about 12. At this pH, however, the solution will begin to thicken and form a gel.

The addition of heavy-metal or alkaline-earth salts to an algin solution also causes it to thicken and gel. At high concentrations, such salts react with algin to precipitate the water-insoluble derivatives. Propylene glycol is resistant to reactions with solutions of the heavy-metal or alkaline-earth salts.

Solutions of algin derivatives of the metallic elements that are amphoteric or that form complexes with ammonia can be prepared by the addition of excess ammonium hydroxide.

As the pH of algin solutions is lowered below about 4.5, the solutions form gels; at about pH 3, alginic acid is precipitated (except from the solutions of propylene glycol alginate).

The use of salts of metals that form insoluble algin derivatives makes it possible to transform fluid algin solutions into firm gels and to obtain any of the intermediate semigelatinous consistencies between these two extremes. The sparingly soluble calcium salts--such as calcium sulfate, calcium gluconate, calcium tartrate, and calcium citrate--are often used for this purpose. The rate of gelation can be controlled by the use of sodium phosphate buffers.

Algin solutions can form films that are clear, tough, and flexible and that have good adherent qualities. Not only are these films resistant to greases, oils, fats, waxes, and organic solvents, but they also

are compatible with the common hydroscopic plasticizers, such as glycerine and sorbitol. They can be made water resistant by the aid of urea-formaldehyde-type resins, which make the films insoluble on heating. They can also be made water resistant by treatment of the films with a solution of an alkaline-earth or heavy-metal salt, such as zinc chloride or zirconium oxychloride. An additional method of making insoluble films is to form a metalic derivative that is soluble in excess ammonium hydroxide. Drying the films drives off the ammonia and makes the films insoluble. The metallic derivatives can be formed from the salts of zinc, aluminum, copper, chromium, and iron.

Carrageenin

Although agar is entirely produced in Southern California and algin is largely produced there, carrageenin is largely produced in exactly the opposite side of the country, in Maine and Massachusetts. Carrageenin accounts for a substantial proportion of the income from the phycocolloids manufactured in the United States.

Use.--One of the more important uses of carrageenin is in the suspension of cocoa fibers in the production of chocolate milk. Another important use is in the stabilizing of ice cream, in which it stops wheying off, controls ice-crystal formation, and gives improved melt-down characteristics. Some additional uses of carrageenin are in the production of milk puddings, pie fillings, frosting mixes, milk shakes and fountain specialties, meringues, whipped-cream stabilizers, sauce thickeners, dietetic salad dressing and low-calorie foods, variegated ice-cream syrups, frozen pops, tooth pastes, pharmaceutical items, hand lotions, cream shampoos, and cold-water paints.

Source.--Carrageenin is produced from Irish moss (Chondrus crispus), which is obtained along the north Atlantic coast particularly from Scituate, Massachusetts; Portland and Rockland, Maine; Yarmouth, Nova Scotia; and Prince Edward Island.

Rhydwen (1954) reports that in 1953 the value of the Irish moss harvested in the Maritime Provinces was $300,000. The Irish moss is found growing from just above low-water level down to a depth of about 20 feet and is relatively easy to harvest. In some areas, it is often collected by the wagonload after it has been washed up on the shore by storms. Usually, however, it is picked by hand or is raked. The rakes have close-set teeth and have handles from 15 to 20 feet long. An experienced man can obtain as much as 800 to 1,000 pounds on a tide. The plants are gathered in bags and sent to a central collection point for drying and baling.

The collecting firms have voluntarily accepted inspection of the Irish moss before shipment. Grade A Irish moss contains not more than 2.5 percent sand, not more than 5 percent other foreign material, and not more than 18 percent moisture.

Method of manufacture.--Godston (1949) has reported on the process of manufacture used by his company.

Properties.--Some of the properties of the water solutions of carrageenin are as follows:

1. They are ionized. (Carrageenin, being an anionic polyelectrolyte, interacts with proteins and other large molecules having positively charged groups.)

2. They are viscous at low colloid concentration.

3. They form gels that are thermally reversible.

4. They stabilize emulsions of both vegetable oil and mineral oil.

5. They suspend solids through the development of a thixotropic system having a yield value greater than the net mass of the particles being suspended. (Thixotropy: the reversible property--exhibited by some gels--of becoming fluid when shaken.)

6. They stabilize foams.

7. They modify the growth of ice crystals through colloidal structure as well as through viscous effect.

8. They bind and hold free moisture, which is important in maintaining softness in certain bakery goods.

9. They are softening and relaxing to living tissues, such as the skin.

10. They control "body" in many food, drug, and cosmetic preparations.

11. They improve "mouth feel," especially of watery liquids.

12. They remove harsh and sharp flavors in certain foods.

SUMMARY

Seaweeds can be classified as green, blue-green, brown, or red. Only the brown and red seaweeds are presently of economic importance. Although the brown and the red seaweeds may grow in the same geographical area, the brown seaweed flourishes in colder water than does the red seaweed. The red seaweeds generally grow in deeper water than do the brown seaweeds. Many of the important seaweeds must be harvested by hand, and the development of mechanical harvesters is one of the important problems of the seaweed industry.

The major constituents in seaweeds are the carbohydrates; the minor constituents include protein, fat, minerals, and vitamins. Seaweeds have long been used for human food in the Orient, whereas this use in the United States has been relatively unimportant. Seaweed meal, at about the 2- or 3-percent level in the rations of farm animals, is said to produce beneficial results. The meal makes a good fertilizer if suitably supplemented with nitrogen and phosphorus, since it is high in potassium.

During World War I, the California kelp industry produced large quantities of potassium chloride, iodine, decolorizing carbon, and such organic solvents as acetone. The seaweeds represent a tremendous reserve source of potassium chloride and iodine.

Other derived products that can be made from seaweed include mannitol, an alcohol having 6 OH groups.

The primary economic value of seaweeds is as sources of the phycocolloids--agar, algin, and carrageenin. These materials are used in making bacteriological solid culture media, dental impression molds, and stabalizers for chocolate milk and in manufacturing hundreds of products as diverse as terramycin suspensions and battery-plate separators. Thus the seaweeds--far from being weeds--are exceedingly useful seaplants.

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